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Theoretical study of the electronic and optical properties of Cu-doped anatase TiO_2 using DFT

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Abstract: Using density functional theory (GGA-PBE) as implemented in CASTEP, we present a first-principles study of Cu-doped anatase TiO_2. Changes in electronic structure and optical response were investigated using a primitive unit cell model with one Ti atom replaced by Cu (at about 5% of doping). Our calculations show that the corresponding charge-density isosurfaces show strong localization around the dopant site, and that Cu incorporation introduces well-defined impurity states around mid-gap, arising mostly due to Cu-3d orbitals. An examination of the complex dielectric function shows that the transitions involving the Cu-induced mid-gap levels are responsible for the noticeable redshift of the optical absorption edge. By extending its photoresponse into the visible spectrum, Cu doping may significantly improve the photocatalytic performance of anatase TiO_2, according to this visible-light activation.

Keyword: Cu-doped TiO_2; Carrier mobility; Carrier lifetime; CASTEP code; Electronic structure; Optical properties.

Introduction

Titanium dioxide (TiO_2) has long been the focus of attention due to its long-term stability, nontoxicity, and photocatalytic activity [1]. However, the wide band gap of anatase (∼3.2) restricts its optical response to the UV region, which represents less than 5% of the solar spectrum at Earth's surface. Researchers have investigated a variety of methods, such as heterojunction formation [2], surface sensitization [3], and non-metal and metal ion doping [4], in an effort to increase visible light activity and capture a greater percentage of sunlight. Among dopants, 3d transition metals are a special kind of dopants that can mediate sub-band gap optical transitions by introducing mid-gap states in energy levels within the TiO_2 band gap [5]. However, if they are not carefully controlled, they also run the risk of forming recombination centers.

Copper (Cu) has become a particularly promising dopant due to its favorable ionic radius and multiple oxidation states, which allow substitutional incorporation into the TiO_2 lattice. Additionally, its d-orbital character can produce mid-gap states that extend light absorption toward the visible region without significantly reducing photogenerated charge carriers [6,7]. Photoluminescence and transient absorption measurements confirm that visible light photo-catalytic activity is enhanced by moderate Cu doping (1–3 at%) [8], while overdoping (>5 at%) mostly results in performance degradation due to increased non-radiative recombination [9]. First-principles calculations indicate that substitutional Cu produces occupied impurity levels that are approximately 0.7–1.2 eV above the valence-band maximum. These levels mainly correspond to Cu 3d–O 2p hybrid orbitals, and enable photon absorption in the 400–550 nm range through electronic transitions from valence to impurity [10].

In this work, we present a detailed first-principles study of the electronic structure and optical properties of Cu-doped TiO_2 using density functional theory with the CASTEP code [11]. We clarify the nature of Cu-induced impurity states and measure their effect on the absorption edge shift by examining the electronic density of states, the mobility and lifetime of charge carriers, and the optical dielectric function. Our results indicate optimal doping levels for improved visible-light harvesting

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and provide atomistic insight into how Cu incorporation modifies the photocatalytic properties of TiO_2 anatase.

Materials and Methods

Our first-principles quantum mechanical calculations were performed using the plane-wave pseudopotential method as implemented by Cambridge Serial Total Energy Package (CASTEP) code. The local density approximation (LDA) with a local functional CA-PZ was used in geometry optimizations [12], while all electronic structure and optical property calculations utilized the generalized gradient approximation (GGA) with gradient-corrected functional Perdew–Burke–Ernzerhof (PBE) form [13]. We also employed Hubbard+U corrections to correct the underestimation of the band gap by PBE. Figure 1 shows (a) the primitive unit cell of TiO_2 anatase and (b) the corresponding Cu-doped structure, in which a single Ti atom has been replaced by a Cu atom ((5%). Ultrasoft pseudopotentials were set to describe core electrons, and the cutoff energy was set to 450 eV after every atomic energy converged to 1.0×10^{-6} eV. Brillouin-zone sampling applied a $4\times4\times4$ Monkhorst–Pack k-point grid for all geometry optimizations. Corrections of DFT+U were applied using the Dudarev approach with U_{eff} values of 6.5 eV for Ti3d, 2.0 eV for O2p, and 2.5 eV for Cu3d states to better describe local Coulomb interactions. A denser $6\times6\times6$ k-point mesh was used for electronic-structure and optical calculations (GGA-PBE+U). Total and projected density of states (DOS/PDOS) employed Gaussian smearing of 0.05 eV. The structural parameters such as the lattice constants are given in Table1 with other previous computational and experimental results [14].

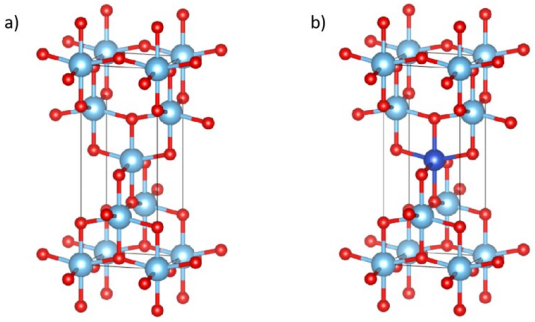

Figure 1. (a) Primitive unit cell of pristine TiO_2 anatase.(b) A single Cu atom substituted form of TiO_2 structure. Blue spheres: Ti; red spheres: O; dark blue sphere: dopant atom.

Table 1. Geometrical data for titanium dioxide TiO_2 anatase doped with a copper atom

Unit cell parameters (Å)	TiO_2	$TiO_{1-x}Cu_xO_2$	Experiment	Deviation (%)
a	3.776	3.775	3.785	+0.23
b	3.776	3.775	3.785	+0.23
c	9.484	9.486	9.514	+0.31
c/a	2.511	2.512	2.513	+0.08

Results

The electronic band structure of the pristine and Cu-doped anatase TiO_2 calculated in our study are shown in Figure 2. The conduction band minimum (CBM) is located at the G point, while the valence band maximum (VBM) is located at the M point, which means that TiO_2 anatase has an indirect band gap [15]. The valence band of pristine TiO_2 mostly consists of 3d states of Ti and 2p, 2s states of O atoms. The material's ability to absorb visible light is limited by the large band gap of 3.2 eV caused by this distinct separation.

Doping with Cu atom, we observe a noticeable decrease in the band gap to 3.08 eV. The Cu 3d states hybridize with the Ti 3d states, forming localized impurity states near the valence band edge as well as the mid-gap states near the Fermi level within the band gap. These new states effectively modify the band gap and introduce additional energy levels that can promote the absorption of low-energy photons, shifting the absorption spectrum into the visible side [6]. However, these localized states can act as recombination centers of charge carriers, making Cu-doped TiO_2 not suitable as a

photocatalytic material [16]. Ultimately, we can determine whether our doped system has enhanced the photocatalytic properties of titanium dioxide by analyzing the changes in charge carrier properties and optical absorption spectra.

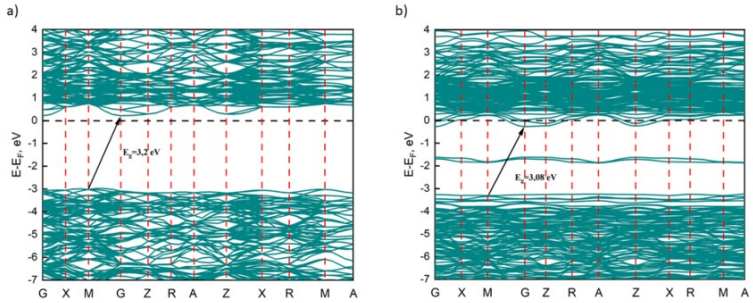

Figure 2. Electronic band structures: (a) pristine TiO_2.(b) Cu-doped TiO_2

The charge carrier mobilities and their lifetimes for both structures are presented in Table2. The carrier mobility, μ, was calculated within the deformation–potential framework according to the equation

$$\mu = \frac{(8\pi)^{1/2}\hbar^4 e C_{ij}}{3(m^*)^{5/2}(k_B T)^{3/2} E_{ij}^2} \tag{1}$$

where

- $\hbar$ is the reduced Planck constant,
- e is the elementary charge,
- C_{ij} is the elastic modulus along the transport direction,
- m^* is the effective mass of the charge carrier,
- k_B is the Boltzmann constant,
- T is the absolute temperature, and
- E_{ij} is the deformation potential constant, describing the shift of the band edge per unit strain.

When Cu is added to the TiO_2 lattice, the electron effective mass increases moderately (from 1.198×10^{-32} kg to 1.334×10^{-32} kg) and the hole effective mass rises significantly (from 1.398×10^{-32} kg to 2.075×10^{-32} kg). Correspondingly, hole mobility in the doped sample falls by roughly 63% (from 1599 $cm^2/V{\cdot}s$ to 596 $cm^2/V{\cdot}s$), while electron mobility decreases by only ∼24% (from 2355 $cm^2/V{\cdot}s$ to 1800 $cm^2/V{\cdot}s$). The tendency for carrier lifetimes is similar: Cu-doping results in a smaller decrease in electron lifetime (from 0.176 to 0.149 ns) and an ≈45% reduction in hole lifetime (from 0.139 to 0.077 ns).

The carrier scattering lifetime can be written in terms of mobility as

$$\tau = \frac{m^* \mu}{q} \tag{2}$$

Hence, for electrons and holes respectively,

$$\tau_e = \frac{m_e^* \mu_e}{q}, \qquad \tau_h = \frac{m_h^* \mu_h}{q} \tag{3}$$

where

- m_e^*, m_h^* are the electron and hole effective masses,
- μ_e, μ_h are the electron and hole mobilities,
- q is the elementary charge.

The more noticeable decline in lifetime and hole transport indicates that Cu-induced states speed up recombination and limit hole mobility. Although Cu-doping narrows the band gap, it severely weakens hole transport while only slightly affecting electrons, so adjusting Cu levels or adding co-catalysts is key to balancing better light absorption with carrier mobility and lifetime.

Table 2. Effective mass, mobility, and carrier lifetime of $TiCuO_2$ and TiO_2 structures

Structure	Effective mass (10^{-32} kg)		Mobility (cm^2/Vs)		Lifetime (10^{-9} s)	
	m_h	m_e	μ_h	μ_e	τ_h	τ_e
TiO_2	1.398	1.198	1599	23655	0.139	0.176
$Ti_{1-x}Cu_xO_2$	2.075	1.334	596.4	1800	0.077	0.149

The polarization-resolved absorption spectra of TiO_2 and Cu-doped $TiO_{1-x}Cu_xO_2$ reveal significant light-harvesting enhancements (Figure 3). For both [001] and [100] directions, Cu doping induces a pronounced redshift of the absorption edge, extending photo-response into the visible region (>2.5 eV). The doped system exhibits substantially enhanced absorption intensity across 2.5–3.5 eV, with peak values exceeding 1.5×10^4 cm^{-1} [10,16,17].

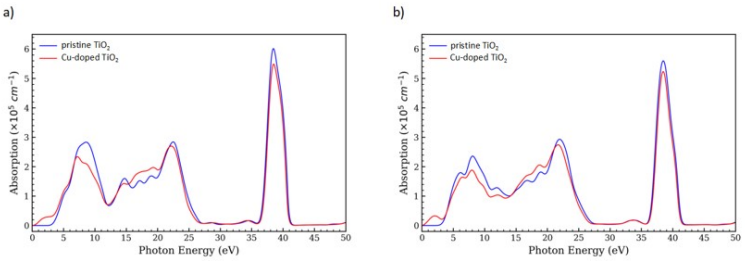

Figure 3. Optical absorption spectrum of pristine and Cu-doped TiO_2 under (a) 001 and (b) 100 polarization directions

Anisotropic characteristics are observed: The [001] polarization shows the strongest en- hancement near the absorption edge (3.0–3.5 eV), indicating preferential electronic modifica- tions along the c-axis. Conversely, the [100] direction displays broader enhancement across the visible spectrum, suggesting more uniform photon capture perpendicular to the c-axis [18]. These modifications confirm effective band structure engineering for visible-light harvesting via Cu doping despite reduced carrier mobility and lifetime.

Conclusions

In this work, first-principles calculations demonstrate that substituting Cu into the TiO_2 lattice ($TiO_{1-x}Cu_xO_2$) effectively narrows the band gap from 3.2 eV to roughly 3.08 eV by introducing Cu 3d–derived mid-gap states, resulting in a pronounced redshift of the absorption edge under both [001] and [100] polarizations. The Cu–doped system exhibits more than a two-fold enhancement in visible-light absorption (2.5–3.5 eV), with absorption coefficients surpassing 1.5×10^4 cm^{-1}. However, the incorporation of Cu also significantly increases the hole effective mass (from 1.398×10^{-32} kg to 2.075×10^{-32} kg) and reduces hole mobility and lifetime by over 60% and 45%, respectively, while electron transport is only modestly affected.

These findings highlight a critical compromise: Cu-doping optimizes light harvesting but at the expense of a decrease in charge-carrier mobility. To fully exploit the enhanced optical response for solar-driven photocatalysis, strategies such as fine-tuning the Cu concentration, employing co-catalysts, or constructing heterostructures are recommended to mitigate charge-carrier recombination and restore balanced carrier dynamics. Future experimental validation of these predictions will be essential to guide the design of high-performance TiO_2-based photocatalysts.

Authors' contribution.

A.A. Azamjonov: Writing - original draft. Sh.I. Mamatkulov: Writing–review editing; Supervision; Project administration; Conceptualization; Funding acquisition.

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Ethics approval.

Since this study does not involve human or animal subjects, ethical review and approval is notrequired. Therefore, ethical approval does not apply to research.

Consent for publication

Human participants were not involved in this study. For this reason, informed consent is notrequired.

Data Availability Statement

All computational data confirming the results presented in this article are held by the authors and presented within the article in the form of the main text and image/table. Additional informationcan be obtained from the author(s)based on a reasoned query.

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Conflict of interest

The authors declare that there is no conflict of interest in this study. There are no personal, financial or other interests that affect the presentation or interpretation of research results.

Abbreviations

DFT	Density Functional Theory
GGA	Generalized Gradient Approximation
PBE	Perdew–Burke–Ernzerhof functional
LDA	Local Density Approximation
CA-PZ	Ceperley–Alder–Perdew–Zunger functional
DOS	Density of States
PDOS	Projected Density of States
CASTEP	Cambridge Serial Total Energy Package
VBM	Valence Band Maximum
CBM	Conduction Band Minimum
eV	electronvolt
Å	ångström
$\hbar$	reduced Planck constant
k_B	Boltzmann constant
T	Temperature
μ	Carrier mobility
τ	Carrier lifetime
m^*	Effective mass
U_{eff}	Effective Hubbard U parameter

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